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TELLURIUM DIOXIDE

[7446-07-3]

Formula: TeO_2 ; MW 159.60

Synonym: tellurous acid anhydride

Uses

Tellurium dioxide is used to prepare tellurium metal, telluric acid, and many tellurium salts.

Physical Properties

White crystals; dimorphic; exists in tetragonal and orthorhombic forms; density 5.75 g/cm³ (tetragonal), 6.04 g/cm³ (orthorhombic); melts at 733°C forming a deep yellow liquid; vaporizes at 1,245°C; insoluble in water; soluble in acids and alkalies.

Thermochemical Properties

ΔH_f°	-77.1 kcal/mol
ΔG_f°	-64.6 kcal/mol
S°	19.0 cal/deg mol
ΔH_{fus}	7.0 ± 0.5 kcal/mol
ΔH_{vap}	51.7 kcal/mol

Production

Tellurium dioxide in its orthorhombic form occurs in nature as mineral tellurite. It is mined from natural deposits. Also, tellurium dioxide is produced as an intermediate during recovery of tellurium metal from anode slimes of electrolytic copper refining (See Tellurium, Production). The dioxide also is prepared by treating tellurium metal with hot nitric acid to form $2\text{TeO}_2 \cdot \text{HNO}_3$. The product then is heated to drive off nitric acid.

Analysis

Elemental composition: Te 79.95%, O 20.05%. The compound can be identified by its physical and x-ray properties. Tellurium content may be measured by digesting the dioxide in HCl or aqua regia, diluting the solution, and analyzing by AA or ICP.

TERBIUM

[7440-27-9]

Symbol Tb; atomic number 65; atomic weight 158.925; a lanthanide series element; an inner-transition rare earth metal; electron configuration $[\text{Xe}]4f^96s^2$; valence states +3, +4; mean atomic radius 1.782Å; ionic radii, Tb^{3+}

0.923Å and 1.04Å corresponding to CN 6 and 8, respectively; standard electrode potential, E° for $\text{Tb}^{3+} + 3e^- \leftrightarrow \text{Tb}$ is -2.28V ; one naturally-occurring stable isotope, Tb-159 (100%); twenty-five artificial radioactive isotopes in the mass range 140–158, 160–165; the longest-lived radioisotope, Tb-158, $t_{1/2}$ 180 years; shortest-lived isotope, Tb-142, $t_{1/2}$ 0.60 sec.

History, Occurrence, and Uses

The element was discovered in 1843 by Carl Gustav Mosander. He determined that the oxide, known as yttria, was actually a mixture of at least three rare earths which he named as yttria—a colorless oxide, erbia—a yellow oxide, and terbia—a rose-colored earth. Mosander separated these three oxides by fractional precipitation with ammonium hydroxide. Pure terbia was prepared by Urbain in 1905. The element was named terbium for its oxide, terbia, which was named after the Swedish town, Ytterby.

Terbium occurs in nature associated with other rare earths. It is found in minerals; xenotime, a rare earth phosphate consisting of 1% terbia; and in euxenite, a complex oxide containing about 1.3% terbia. It also is found in cerite, monazite, and gadolinite. Also, the element has been detected in stellar matter. Abundance of terbium in the earth's crust is estimated to be 1.2 mg/kg.

The metal or its salts do not have any important uses at present.

Physical Properties

Silvery-gray metal; hexagonal crystal structure; malleable, ductile, and soft enough to be cut with a knife; density 8.223 g/cm^3 ; melts at $1,359^\circ\text{C}$; vaporizes at $3,221^\circ\text{C}$; resistivity $116 \times 10^{-6}\text{ ohm-cm}$ at 25°C ; Young's modulus $5.75 \times 10^{11}\text{ dynes/cm}^2$ (from velocity of sound measurements); shear modulus 2.28 dynes/cm^2 ; Poisson's ratio 0.261; thermal neutron absorption cross section, 46 barns; insoluble in water; soluble in acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	92.9 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	83.6 kcal/mol
S° (cry)	17.5 cal/deg mol
S° (gas)	48.6 cal/deg mol
C_p (cry)	6.91 cal/deg mol
C_p (gas)	5.87 cal/deg mol
ΔH_{fus}	2.43 kcal/mol
Thermal conductivity	0.111 W/cm K
Coefficient of linear expansion	$10.3 \times 10^{-6}/^\circ\text{C}$

Preparation

Terbium is recovered from the minerals, monazite, xenotime, and euxenite. The recovery processes are quite similar to those of other lanthanide elements (See individual lanthanide elements). The metal is separated from other rare

earths by ion exchange methods, which are relatively easy and faster than fractional crystallization techniques.

Terbium metal is obtained from its anhydrous trifluoride, TbF_3 , or trichloride, TbCl_3 , by thermal reduction with calcium, carried out in a tantalum crucible. Terbium produced by such methods may contain traces of calcium and tantalum. High purity metal can be prepared by various methods such as vacuum remelting, distillation, amalgam formation, floating zone melting, and various chemical processes.

Compounds

The most common valence state in solid compounds is +3. A +4 valence state is known for the metal in its dioxide, TbO_2 , and tetrafluoride, TbF_4 . Terbium also forms several nonstoichiometric oxides of approximate composition Tb_4O_7 .

In solution the metal exists only in trivalent state, $[\text{Tb}(\text{H}_2\text{O})_n]^{3+}$. The standard electrode potential for $\text{Tb} \rightarrow \text{Tb}^{3+} + 3\text{e}^-$ is calculated to be about 2.39V.

Terbium forms binary compounds with a number of elements including hydrogen, halogens, nitrogen, phosphorus, sulfur, carbon, silicon, selenium, tellurium, boron, arsenic, and antimony. A few well-characterized binary compounds include the four oxides—the cubic crystalline TbO_2 , the body-centered cubic crystalline sesquioxide Tb_2O_3 , the rhombohedral Tb_7O_{12} , and the triclinic $\text{Tb}_{11}\text{O}_{20}$; the hydrides—a cubic dihydride, TbH_2 and a hexagonal trihydride, TbH_3 ; and the cubic crystalline sulfide, nitride, phosphide, selenide, and telluride of compositions TbS , TbN , TbP , TbSe , and TbTe respectively. Halide compounds include orthorhombic trifluoride, TbF_3 ; monoclinic tetrafluoride, TbF_4 ; and the hexagonal triiodide, TbI_3 . Also, several borides and carbides of hexagonal, tetragonal, and cubic structures are known.

Among Tb oxo salts are the monoclinic nitrate hexahydrate $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, the tetragonal oxychloride, TbOCl , and the rhombohedral oxyfluoride, TbOF .

Analysis

Terbium may be identified by various instrumental techniques including atomic absorption and emission spectrophotometry and neutron activation analysis.

THALLIUM

[7440-28-0]

Symbol Tl; atomic number 81; atomic weight 204.38; a Group III A (Group 13) metallic element placed below indium; electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$; valence state +1, +3; atomic radius 1.70Å; standard electrode potential, E° for $\text{Tl}^{3+} + 3\text{e}^- \leftrightarrow \text{Tl}$ is 0.741 V; two naturally-occurring stable isotopes: Tl-203 (29.524%), Tl-205 (70.476%), twenty-eight artificial radioisotope in the mass range 179, 182-202, 204, 206–210; longest-lived isotope, Tl-204, $t_{1/2}$ 3.78 year; shortest-lived isotope, Tl-179 $t_{1/2}$ 0.2 sec.

History, Occurrence, and Uses

Thallium was discovered spectroscopically by Sir William Crookes in 1861. While searching for tellurium, he observed a beautiful green line in the spectrum of residues of a German sulfuric acid manufacturing plant. He named this element after the Latin word *thallos* meaning the budding green twig. In the following year, in 1862, both Crookes and Lamy independently isolated the metal.

Thallium occurs in nature in potash minerals and many sulfide ores. It is found in pyrites from which the metal is recovered. The metal also occurs in the minerals cooksite, lorandite, and hutchinsonite. The average concentration of thallium in the earth's crust is estimated to be 0.85 mg/kg.

Thallium and its compounds have limited applications. It is used in insecticides and rodenticides. Thallium-mercury alloys are used for switches and closures for use at sub-zero temperatures. Another application is in making low melting glasses for electronic encapsulation. Thallium sulfide is used in photocells.

Physical Properties

Metallic luster when freshly cut but attains a bluish-gray tinge on exposure to air resembling lead in appearance; tetragonal crystals; density 11.85 g/cm³ at 20°C; melts at 303.5° C; vaporizes at 1473° C; electrical resistivity 18 microhm-cm at 0°C and 74 microhm-cm at 303°C; tensile strength 1300 psi; surface tension at 327°C, 401 dynes/cm; insoluble in water; soluble in nitric and sulfuric acids; slightly soluble in hydrochloric acid.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	43.55 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	35.24 kcal/mol
S° (cry)	15.45 cal/deg mol
S° (gas)	43.22 cal/deg mol
C_p (cry)	6.29 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	4.02 kcal/mol
Thermal conductivity at 27°C	0.461 W/cm K
Coefficient of linear expansion (at 25°C)	29.9x10 ⁻⁶ /°C

Production

Thallium is recovered from roasting pyrites as a by-product of making sulfuric acid. Also, it is obtained from smelting lead and zinc ores. Lead and zinc concentrates contain small quantities of thallium. During smelting operation at high temperatures thallium compounds volatilize. Thallium compounds, usually oxide and sulfate, are collected in flue dusts along with other metals including selenium, tellurium, cadmium, and indium.

Separating thallium compounds from other substances in flue dust is based on differences in solubility. Solubility differences of thallium salts from those

of other metal salts of the same anions in water, acids, and alkalies, are fully utilized in all separation processes. Two industrial processes are briefly mentioned below (Howe, H.E. 1968. *Thallium*. In *An Encyclopedia of Chemical Elements*, ed. C. E. Hempel, New York, Reinhold Book Corporation). In general, thallium compounds are separated and obtained as by-products during processing and recovery of associated metals in flue dust. For example, thallium is obtained as a by-product in recovering cadmium. In this process, crude flue dust is treated with sulfuric acid which converts both cadmium and thallium to their sulfates. Impurity metals are removed from this solution as their sulfides. The solution then is electrolyzed to form a deposit of cadmium-thallium alloy containing less than 20% thallium. The alloy is treated with boiling water. Thallium is converted to its soluble hydroxide. Any cadmium present in the solution is removed by precipitation with sodium carbonate. Insoluble cadmium carbonate is filtered leaving thallium carbonate in solution. Treating this solution with sodium sulfide precipitates thallium sulfide. The precipitate is dissolved in sulfuric acid to form pure thallium sulfate. The solution then is electrolyzed. Thallium is electrodeposited as sponge on aluminum cathodes.

In another industrial process, flue dusts from smelting lead and zinc concentrates are boiled in acidified water. Thallium dissolves and is separated from insoluble residues by filtration. Dissolved thallium in solution then is precipitated with zinc. Thallium is extracted from the precipitate by treatment with dilute sulfuric acid which dissolves the metal. The solution may also contain zinc, cadmium, lead, copper, indium, and other impurities in trace amounts. These metals are precipitated with hydrogen sulfide. The pure thallium sulfate solution then is electrolyzed to yield thallium.

Reactions

Thallium forms all its compounds in two valence states, +1 (thallous) and +3 (thallic). The metal oxidizes slowly in air at ambient temperature but rapidly on heating, forming thallous oxide, Tl_2O . This oxide oxidizes further on heating to form thallic oxide, Tl_2O_3 . When exposed to air at ambient temperatures for several days thallium forms a heavy oxide crust.

Thallium reacts with water containing oxygen to form thallous hydroxide, $TlOH$, which is a relatively strong base, absorbing carbon dioxide and attacking glass.

The metal dissolves in nitric and sulfuric acid. The solution on evaporation crystallizes to yield thallous nitrate and sulfate. Reaction with hydrochloric acid is very slow.

Thallium burns in fluorine with incandescence. Reactions with other halogens form halides. Thallium combines with several elements forming binary compounds.

Analysis

Thallium may be analyzed by flame- and furnace- AA spectrophotometric methods and also by the ICP-AES methods. For the flame-AA analysis, an air-acetylene flame is satisfactory. The ICP-AES measurement may be carried

out at wavelength 190.86 nm or at 377.57 nm.

Toxicity

Thallium and its compounds (particularly soluble salts) can cause serious or fatal poisoning from accidental ingestion or external application. Acute symptoms are nausea, vomiting, diarrhea, weakness, pain in extremities, convulsions, and coma. Chronic effects are weakness, pain in extremities, and rapid loss of hair. Thallium and its compounds are listed under Federal toxics regulations. It is listed by the US EPA as a priority pollutant metal in the environment.

THALLIUM CHLORIDE

[7791-12-0]

Formula: TlCl ; MW 239.84

Synonym: thallos chloride

Uses

Thallium chloride is a catalyst in chlorination reactions.

Physical Properties

White crystalline powder; turns violet on exposure to light; density 7.004 g/cm^3 at 20°C ; melts at 430°C ; vaporizes at 720°C ; vapor pressure 20 torr at 550°C ; slightly soluble in water, 0.29 g/mL at 15.6°C ; sparingly soluble in boiling water, 2.4 g/100mL ; insoluble in alcohol, acetone and ammonium hydroxide.

Thermochemical Properties

ΔH_f° (cry)	-48.8 kcal/mol
ΔH_f° (gas)	-16.2 kcal/mol
ΔG_f° (cry)	-44.2 kcal/mol
S° (cry)	26.6 cal/deg mol
C_p (cry)	12.2 cal/deg mol
ΔH_{fus}	4.25 cal/deg mol
ΔH_{vap}	24.4 cal/deg mol

Preparation

Thallium chloride may be prepared by heating the metal with chlorine.

Analysis

Elemental composition: Tl 85.22%, Cl 14.78%. A small amount of the salt is dissolved in water (it is slightly soluble in water at room temperature) and the solution analyzed for chloride ion by ion chromatography or by titration with a standard solution of silver nitrate using potassium chromate indicator. The salt is digested with nitric acid, diluted, and analyzed for thallium metal by

flame or furnace AA or ICP-AES (see Thallium).

Toxicity

Thallium chloride is highly toxic. Acute toxic effects are those of thallium poisoning.

THALLIUM FLUORIDE

[7789-27-7]

Formula: TlF; MW 223.38

Synonym: thallos fluoride

Uses

The compound is used in preparing fluoro esters.

Physical Properties

Hard shiny crystals; orthorhombic structure; density 8.23 g/cm³ at 4°C; melts at 327°C; begins to sublime at 300°C; vaporizes at 655°C; very soluble in water, 78.6 g/100mL at 15°C; decomposes in hot water; slightly soluble in alcohol.

Thermochemical Properties

ΔH_f° -18.5 kcal/mol

Preparation

Thallium fluoride is prepared by reacting thallium carbonate with hydrofluoric acid. Also, the compound can be made by reacting thallium metal with fluorine.

Analysis

Elemental composition: Tl 91.49%, F 8.51%. An appropriately diluted aqueous solution may be analyzed for thallium by AA or ICP methods (See Thallium) and for the F⁻ ion by the fluoride ion-specific electrode or by ion chromatography.

Toxicity

Highly toxic (See Thallium).

THALLIUM NITRATE

[10102-45-1]

Formula: TlNO₃; MW 266.39

Synonyms: thallos nitrate; thallium(I) nitrate.

Uses

The salt is an analytical reagent for measuring iodine in the presence of chlorine and bromine. Also, it is used in pyrotechnics and producing green fire for signaling at sea.

Physical Properties

White crystals; exists in three allotropic modifications: a rhombohedral gamma form that transforms to trigonal beta form at 75°C, the trigonal converting to a cubic alpha form at 145°C.

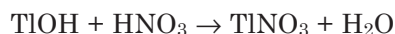
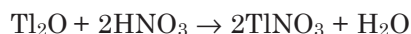
Density of the salt is 5.56 g/cm³; melts at 206°C; vaporizes at 450°C with decomposition; moderately soluble in water, 9.55 g/100mL at 20°C; insoluble in alcohol.

Thermochemical Properties

ΔH_f°	-58.3 kcal/mol
ΔG_f°	-36.4 kcal/mol
S°	38.4 cal/deg mol
C_p	23.8 cal/deg mol
ΔH_{fus}	2.29 kcal/mol

Preparation

Thallium nitrate is prepared by reacting thallium metal, thallous oxide, Tl₂O or thallous hydroxide, TlOH, with nitric acid followed by crystallization:

**Analysis**

Elemental composition: Tl 76.72%, N 5.26%, O 18.02%. An aqueous solution of the salt is analyzed for thallium metal by AA or ICP methods and nitrate ion by electrode, ion chromatography or colorimetric methods.

THALLIUM OXIDE

[1314-12-1]

Formula: Tl₂O; MW 424.707

Synonyms: thallous oxide; thallium (I) oxide

Uses

Thallium oxide is used in manufacturing high coefficient of refraction optical glass (thallium flint glass). Also, the oxide is used to make synthetic gems.

Physical Properties

Black powder; orthorhombic crystals; hygroscopic; density 9.52g/cm³; melts

at 596°C; vaporizes at about 1,080°C; soluble in water, alcohol and acids.

Thermochemical Properties

ΔH_f°	-42.7 kcal/mol
ΔG_f°	-35.2 kcal/mol
S°	30.0 cal/deg mol

Preparation

Thallium oxide can be made by heating Tl metal in air or oxygen. The brown-black thallic oxide, Tl_2O_3 , that may also form begins to lose oxygen at about 100°C converting to thallium oxide, Tl_2O .

Thallium oxide also can be prepared by thermal dissociation of thallium hydroxide, $TlOH$ or thallium carbonate, Tl_2CO_3 . Thallium oxide dissolves in water forming thallic hydroxide, $TlOH$. It reacts with carbon dioxide to form thallic carbonate, Tl_2CO_3 .

Reactions

Thallium oxide slowly oxidizes to thallic oxide, Tl_2O_3 on exposure to air, gradually becoming insoluble in aqueous solution.

Analysis

Elemental composition: Tl 96.23%, O 3.77%. Thallium may be measured by various instrumental methods on an aqueous or acid solution of the metal oxide. Also, the compound can be identified by its physical and x-ray properties. Thallic oxide reverts to thallium oxide on heating above 100°C.

THORIUM

[7440-29-1]

Symbol Th; atomic number 90; atomic weight 232.04; an actinide series radioactive element; electron configuration $[Rn]6d^27s^2$; valence state +4; atomic radius 1.80 Å; ionic radius, Th^{4+} 1.05 Å for coordination number 8; standard electrode potential, E° for $Th^{4+} + 4e^- \leftrightarrow Th$ is -1.899V; all isotopes are radioactive; the only naturally-occurring isotope, Th-232, $t_{1/2}$ 1.4×10^{10} year; twenty-six isotopes are known in the mass range 212-237.

History, Occurrence, and Uses

The element was discovered by Berzelius in 1828. He named it thorium after Thor, the ancient Scandinavian god of war. An important application of thorium came in 1884 when Auer von Welsbach developed the incandescent gas light mantle using thorium oxide as the primary ingredient. The mantle emitted brilliant white light. With this discovery, the mantle industry saw a dramatic growth and a search for new thorium deposits, and thorium production increased sharply. Around the first quarter of the 20th century, electricity had almost replaced the gaslights causing a decline in thorium production. With development of atomic energy in the early 1940s and the use of thorium

as nuclear fuel, thorium production has gone up tremendously.

Large thorium deposits have been found in many parts of the world. It occurs in minerals thorite, ThSiO_4 , and thorianite, $\text{ThO}_2 \cdot \text{UO}_2$. Thorium also is found in mineral monazite which contains between 3 to 9% ThO_2 . ThO_2 is the principal source of commercial thorium. Abundance of thorium in earth's crust is estimated at about 9.6 mg/kg. Thorium and uranium are believed to have contributed much of the internal heat of the earth due to their radioactive emanations since earth's formation.

The principal use of thorium is as a nuclear fuel. When bombarded with excess neutrons it converts to fissionable uranium-235. Another major application is the Welsbach incandescent mantle mentioned earlier. Such mantles are used as portable gaslights. Thorium alloyed with magnesium imparts high strength and creep resistance to magnesium at elevated temperatures. Such alloys are used in vehicles and aerospace equipment. Thorium oxide coated tungsten filaments are used in incandescent lamps, and rods are employed as electrodes in arc-melting. Other uses are in photoelectric cells; as a target in x-ray tubes; and as a reducing agent in metallurgy. Thorium oxide has several industrial applications (See Thorium Oxide).

Physical Properties

Grayish-white lustrous metal; soft when pure; quite ductile and malleable; can be shaped by cold or hot rolling, swaging or drawing; dimorphic, face-centered cubic crystals changing to body-centered cubic structure at $1,400^\circ\text{C}$; density 11.72 g/cm^3 ; melts at $1,750^\circ\text{C}$; vaporizes at $4,788^\circ\text{C}$; electrical resistivity 14 microhm-cm ; Young's modulus $10.3 \times 10^6 \text{ psi}$; shear modulus $4.1 \times 10^6 \text{ psi}$; Poisson's ratio 0.27; soluble in hydrochloric and sulfuric acids, and aqua regia; slightly soluble in nitric acid; insoluble in water.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	143.0 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	133.26 kcal/mol
S° (cry)	12.76 cal/deg mol
S° (gas)	45.42 cal/deg mol
C_p (cry)	6.53 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	3.30 kcal/mol
ΔH_{vap}	140 kcal/mol
Thermal conductivity (at 27°C)	0.540 W/cmK
Coefficient of linear expansion	$11.0 \times 10^{-6}/^\circ\text{C}$

Production

Thorium is recovered mostly from monazite, which is a phosphate mineral of the light-weight rare earths. Monazite occurs as sand associated with silica and a few other minerals in smaller proportions.

The first step in the recovery process involves breaking down or opening up

the ore. This usually is done by one of two methods: (1) digesting with hot concentrated sulfuric acid or (2) treatment with hot concentrated sodium hydroxide. In the acid digestion process, finely-ground monazite is treated with hot sulfuric acid. Thorium and rare earths dissolve in the acid. Phosphoric acid is released from monazite (a phosphate mineral) by reacting phosphates with sulfuric acid. Insoluble residues are removed by filtration. In the caustic digestion process, monazite, on heating with a concentrated solution of sodium hydroxide, breaks down to form soluble trisodium phosphate and an insoluble residue containing hydrated oxides of thorium and rare earths. Thus, in the caustic process, trisodium phosphate is recovered as a by-product. The hydrated oxides are dissolved in sulfuric acid.

Thorium sulfate, being less soluble than rare earth metals' sulfates, can be separated by fractional crystallization. Usually, solvent extraction methods are applied to obtain high purity thorium and for separation from rare earths. In many solvent extraction processes, an aqueous solution of tributyl phosphate is the extraction solvent of choice.

There are several processes for commercial thorium production from monazite sand. They are mostly modifications of the acid or caustic digestion process. Such processes involve converting monazite to salts of different anions by combination of various chemical treatments, recovery of the thorium salt by solvent extraction, fractional crystallization, or precipitation methods. Finally, metallic thorium is prepared by chemical reduction or electrolysis. Two such industrial processes are outlined briefly below.

Finely-ground monazite is treated with a 45% NaOH solution and heated at 138°C to open the ore. This converts thorium, uranium, and the rare earths to their water-insoluble oxides. The insoluble residues are filtered, dissolved in 37% HCl, and heated at 80°C. The oxides are converted into their soluble chlorides. The pH of the solution is adjusted to 5.8 with NaOH. Thorium and uranium are precipitated along with small quantities of rare earths. The precipitate is washed and dissolved in concentrated nitric acid. Thorium and uranium are separated from the rare earths by solvent extraction using an aqueous solution of tributyl phosphate. The two metals are separated from the organic phase by fractional crystallization or reduction.

In one acid digestion process, monazite sand is heated with 93% sulfuric acid at 210°C. The solution is diluted with water and filtered. Filtrate containing thorium and rare earths is treated with ammonia and pH is adjusted to 1.0. Thorium is precipitated as sulfate and phosphate along with a small fraction of rare earths. The precipitate is washed and dissolved in nitric acid. The solution is treated with sodium oxalate. Thorium and rare earths are precipitated from this nitric acid solution as oxalates. The oxalates are filtered, washed, and calcined to form oxides. The oxides are redissolved in nitric acid and the acid solution is extracted with aqueous tributyl phosphate. Thorium and cerium (IV) separate into the organic phase from which cerium (IV) is reduced to metallic cerium and removed by filtration. Thorium then is recovered from solution.

Thorium metal may be produced from its salts—usually the oxide or a halide—by several methods that include electrolysis and reduction with calci-

um. In the calcium reduction process, thorium oxide is heated in a closed vessel at 950°C. The product is cooled and leached with water and dilute acid and then washed and vacuum-dried to form a free-flowing powder.

Thorium metal also can be prepared by thermal reduction of its halides with calcium, magnesium, sodium, or potassium at elevated temperatures (950°C), first in an inert atmosphere and then in vacuum. Fluoride and chloride thorium salts are commonly employed. Berzelius first prepared thorium by heating tetrachloride, ThCl_4 , with potassium. Magnesium and calcium are the most common reductant. These metals are added to thorium halides in excess to ensure complete reduction. Excess magnesium or calcium is removed by heating at elevated temperatures in vacuum. One such thermal reduction of halides produces thorium sponge, which can be converted into the massive metal by melting in an electron beam or arc furnace.

Thorium can be obtained from its halides by electrolysis. A fused salt bath of NaCl-KCl-ThCl_4 or NaCl-KCl-KF-ThF_4 or similar eutectic mixtures is employed in electrolysis. The electrolysis may be carried out in a graphite crucible, and thorium is deposited as a coarse powder on the electrode, which is made of molybdenum or other suitable material.

Reactions

Thorium combines with practically all nonmetallic elements except noble gases, forming binary compounds. The most stable oxidation state is +4. Heating the metal in air or oxygen forms the oxide, ThO_2 . Heating the metal in hydrogen at 600°C yields the dihydride ThH_2 . Also, higher halides of thorium are known. They are produced by heating the dihydride in hydrogen at 250°C. Thorium hydrides are pyrophoric.

Thorium combines with nitrogen at elevated temperatures to form nitrides ThN and Th_2N_3 . Reaction with carbon at elevated temperatures forms the carbides ThC and ThC_2 .

Thorium reacts with all halogens forming tetrahalides.

Thorium also forms inter-metallic compounds with iron, copper, aluminum, selenium, nickel, cobalt, manganese, bismuth, and many other metals at elevated temperatures.

Nuclear Reactions

Thorium undergoes radioactive disintegration through several decay steps ending by forming stable lead-208. The decay series involves six alpha and four beta emission steps. Radon-220 (thoron), an alpha emitter, is one of the disintegration products in the series.

Neutron bombardment converts thorium-232 to its isotope of mass 233. The thorium-233 formed undergoes two successive beta decays to form uranium-233, a fissionable material, similar to uranium-235 and plutonium-239.

Toxicity

All thorium isotopes are radioactive. Also all its intermediate decay products including radon-220 are radioactive and present radiation hazard. Exposure can cause cancer.

THORIUM DIOXIDE

[1314-20-1]

Formula: ThO_2 ; MW 264.04

Synonyms: thorium oxide; thorium anhydride; thoria

Occurrence and Uses

Thorium dioxide occurs in nature as mineral thorianite. Thorium dioxide is used in gaslight mantles, in tungsten filaments for incandescent lamps, to improve efficiency of electronic tubes, and in thoriated tungsten rods as electrodes in arc melting. An important application of this compound is hardening nickel to impart high strength and corrosion resistance at high temperatures. It also is used in making nonsilicate optical glass of high refractive index and low dispersion, and in special refractory crucibles. Thorium dioxide is a catalyst in many chemical reactions including petroleum cracking, conversion of ammonia to nitric acid, and preparation of sulfuric acid.

Physical Properties

White cubic crystals; refractive index 2.200 (thorianite); density 10.0 g/cm³; hardness 6.5 Mohs; melts at 3,390°C; vaporizes at 4,400°C; insoluble in water or alkalis; soluble in acids with difficulties.

Thermochemical Properties

ΔH_f°	-293.1 kcal/mol
ΔG_f°	-279.4 kcal/mol
S°	15.6 cal/deg mol
C_p	14.8 cal/deg mol

Preparation

Thorium dioxide is obtained as an intermediate in the production of thorium metal from monazite sand (See Thorium).

The compound also can be prepared by many other methods including thermal decomposition of thorium oxalate, hydroxide, carbonate, or nitrate. Heating thorium metal in oxygen or air, and hydrolysis of thorium halides also yield thorium dioxide.

Analysis

Elemental composition: Th 87.88%, O 12.12%. The oxide may be identified by x-ray methods. Thorium dioxide may be analyzed by AA or ICP after digestion in aqua regia and appropriate dilution in water.

THORIUM NITRATE

[13823-29-5]

Formula: $\text{Th}(\text{NO}_3)_4$; MW 480.06; forms a stable tetrahydrate, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$

[33088-16-3], MW 552.12, the commercial form of the nitrate; also exists as hexa- and dodecahydrates, $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$, respectively.

Uses

Thorium nitrate is a reagent for measuring fluorine and for making thoriated tungsten filaments. Thorium nitrate containing 1% cerium nitrate is the impregnating liquid in making incandescent gas mantles.

Physical Properties

The tetrahydrate is a white crystalline mass; hygroscopic; decomposes at about 500°C; very soluble in water; soluble in ethanol.

Preparation

Thorium nitrate is obtained as an intermediate in making thorium metal from monazite sand. Also, the salt is prepared by heating thorium metal or its oxide or hydroxide with nitric acid, followed by evaporation of the solution and crystallization.

Analysis

Elemental composition (in anhydrous salt): Th 48.33%, N 11.67%, O 40.00%. The aqueous solution may be analyzed for thorium (See Thorium) and for nitrate ion by ion chromatography, nitrate ion-specific electrode, and colorimetric methods. The water of crystallization can be determined by DTA, TGA, and other gravimetric methods.

Toxicity

Thorium nitrate is highly toxic by ingestion and other routes of exposure. The compound also is a radiation hazard.

THULIUM

[7440-30-4]

Symbol Tm; atomic number 69; atomic weight 168.93; a lanthanide series element; a rare earth metal; electron configuration $[\text{Xe}]4f^{13}6s^2$; valence +2, +3; atomic radius 1.73 Å; ionic radius, Tm^{3+} 1.09 Å for coordination number 7; one stable, natural isotope Tm-169 (100%); thirty radioisotopes in the mass range 146-168, 170-176; $t_{1/2}$ 1.92 years.

History, Occurrence, and Uses

Thulium was discovered in 1879 by Cleve and named after Thule, the earliest name for Scandinavia. Its oxide thulia was isolated by James in 1911. Thulium is one of the least abundant lanthanide elements and is found in very small amounts with other rare earths. It occurs in the yttrium-rich minerals: xenotime, euxenite, samarskite, gadolinite, loparite, fergusonite, and yttrionparisite. Also, it occurs in trace quantities in minerals monazite and

apatite. Abundance of thulium in earth's crust is estimated to be 0.52 mg/kg. The metal has very few commercial applications because of its high cost and low relative abundance. Thulium metal pellets containing natural isotope 169 and radioactive Tm-170 are used in portable x-ray equipment as medical and dental diagnostic tools. These pellets also are used to detect flaws in small, inaccessible parts of mechanical and electrical devices. Radioactive thulium-171 is a beta emitter with a half-life of two years and potentially is useful as an energy source. Natural thulium is used in ceramic magnetic materials (ferrites) for microwave devices.

Physical Properties

Silvery-white lustrous metal; hexagonal close-packed structure; density 9.321 g/cm³ at 25°; melts at 1,545°C; vaporizes at 1,947°C; electrical resistivity 79 microhm-cm; compressibility 2.6×10⁶ cm²/kg; effective magnetic moment 7.62 Bohr magneton; insoluble in water; dissolves in concentrated acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	55.5 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	47.2 kcal/mol
S° (cry)	17.7 cal/deg mol
S° (gas)	45.4 cal/deg mol
C_p (cry)	6.46 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	4.02 kcal/mol
Thermal conductivity (at 27°C)	0.169 W/cmK
Coefficient of linear expansion	13.3×10 ⁻⁶ /°C

Production

Thulium is recovered from xenotime, gadolinite, euxenite, samarskite, and other minerals. The first step of recovery involves opening the ores. If xenotime, (Y)PO₄ is the starting material, the mineral is heated with an excess of sulfuric acid (95%). The product mixture is treated with cold water to separate water-soluble sulfates from unreacted mineral, silica, and other insoluble residues. The solution is filtered and yttrium and the individual rare earths are separated from this solution by ion exchange. The tripositive lanthanide metal ions and yttrium are absorbed on an appropriate cation exchange column and eluted with ammonium ethylenediamine tetraacetic acid (EDTA) at pH 8.4. The cation-exchange resin is pretreated with an equimolar mixture (1 M) of copper sulfate-sulfuric acid. The various eluate fractions are collected, and are treated with oxalic acid. The metals are precipitated as oxalates. Precipitate from the thulium fraction is calcined at 800°C to convert oxalate into oxide, Tm₂O₃.

If thulium is to be recovered from gadolinite, Be₂Fe(Y)₂Si₂O₁₀, pulverized mineral is opened by digesting with hot nitric acid-hydrochloric acid mixture.

Insoluble silica residues are removed by filtration. The solution now contains beryllium, iron, yttrium, and the rare earths. The solution is treated with oxalic acid to precipitate yttrium and the rare earths. The precipitate is calcined at 800°C to form rare earth oxides. The oxide mixture is dissolved in an acid from which yttrium and the rare earths are separated by the ion-exchange as above. Caustic fusion may be carried out instead of acid digestion to open the ore. Under this condition silica converts to sodium silicate and is leached with water. The insoluble residue containing rare earths and yttrium is dissolved in an acid. The acid solution is fed to an ion exchange system for separating thulium from other rare earths.

Thulium metal is prepared from its oxide by reduction with lanthanum at its melting point of 1,545°C. Thulium is separated from lanthanum by sublimation in vacuum. The metal vapor is condensed into crystalline metal in purified form free from lanthanum.

Reactions

The most stable oxidation state of thulium is +3. Only the tripositive Tm^{3+} ion is encountered in aqueous media. The metal also forms compounds in +2 and +4 valence states, but there is no evidence of Tm^{2+} and Tm^{4+} existing in aqueous phase. Thulium is relatively stable in air at ambient temperature. However, it combines with oxygen on heating forming its sesquioxide, Tm_2O_3 .

Reactions with halogens are slow at ordinary temperatures, but vigorous above 200°C, forming trihalides.

Thulium reacts with concentrated mineral acids forming corresponding salts and liberating hydrogen.

The metal forms binary compounds when heated at elevated temperatures. Such binary compounds of thulium are known with many nonmetallic and metallic elements having varying stoichiometric compositions, such as TmN , TmS , TmC_2 , Tm_2C_3 , TmH_2 , TmH_3 , TmSi_2 , TmGe_3 , TmB_4 , TmB_6 , and TmB_{12} .

Analysis

Thulium may be determined by atomic absorption and emission spectrophotometry. The metal and its compounds are dissolved in acids and diluted appropriately before analysis. Thulium also can be measured by neutron activation analysis.

[7440-31-5]

Symbol Sn; atomic number 50; atomic weight 118.69; a Group IV A (Group 14) metallic element of carbon family; electron configuration $[\text{Kr}] 4d^{10}5s^25p^2$; valence states +2, +4; atomic radius 1.41Å; electronegativity 1.7; standard electrode potential, E° for $\text{Sn}^{2+} + 2e^- \leftrightarrow \text{Sn}$ is -0.1375 V; ten naturally-occurring sta-

ble isotopes: Sn-112 (0.97%), Sn-114 (0.65%), Sn-115 (0.34%), Sn-116 (14.54%), Sn-117 (7.68%), Sn-118 (24.22%), Sn-119 (8.59%), Sn-120 (32.59%), Sn-122 (4.63%), Sn-124 (5.79%); twenty-five radioisotopes in the mass range 100-111, 113, 121, 123, 125-134; the longest-lived isotope, Sn-126, $t_{1/2}$ 1.0×10^5 years.

History, Occurrence and Uses

Tin is known from ancient times. Its alloy, bronze, containing 10 to 15% tin has been in use in weapons and tools for millennia.

The most important mineral of tin is cassiterite, SnO_2 . It occurs in the form of alluvial sand. Also, it is found embedded in granite rocks. Other tin-bearing minerals are stannite and tealite. Abundance of tin in the earth's crust is estimated to be 2.3 mg/kg. Tin is used for plating steel to make "tin cans" for preserving food. Also, tin is coated over other metals to prevent corrosion. An important application of tin is to produce float glass, made by floating molten glass on molten tin which is used for windows. A number of tin alloys have wide industrial applications and include bronze, solder, Babbit metal, White metal, type metal, fusible metal, and phosphor bronze. A tin-niobium alloy that is superconducting at low temperatures is used in constructing super magnets. Tin also is in wrapping foil and collapsible tube.

Physical Properties

Silvery-white metal at ordinary temperature; slowly changes to gray below 13.2°C ; soft, malleable, and somewhat ductile; Brinell hardness 2.9.

Tin has two allotropic forms: (1) white tin, the beta form, and (2) gray tin, the alpha form. The white tin (beta form) has a tetragonal structure. When cooled below 13.2°C , its color slowly changes from white to gray, the beta allotrope converting to alpha (gray tin). The presence of small amounts of antimony or bismuth prevents this transformation from white to gray tin. Other impurities such as zinc or aluminum promote change from white to gray tin.

Some other physical properties are: density 7.28 g/cm^3 (white), 5.75 g/cm^3 (gray) and 6.97 g/cm^3 (liquid at the melting point); melts at 231.9°C ; vaporizes at $2,602^\circ\text{C}$; electrical resistivity 11.0 and 15.5 microhm-cm at 0 and 100°C , respectively; viscosity 1.91 and 1.38 centipoise at 240 and 400°C , respectively; surface tension 5.26 and 5.18 dynes/cm at 300 and 400°C , respectively; modulus of elasticity $6 - 6.5 \times 10^6$ cgs psi; magnetic susceptibility 0.027×10^{-6} cgs units; thermal neutron absorption cross section 0.625 barns; insoluble in water; soluble in HCl , H_2SO_4 , aqua regia, and alkalies; slightly soluble in dilute nitric acid

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})(\text{white})$	0.0
$\Delta H_f^\circ(\text{cry})(\text{gray})$	-0.50 kcal/mol
$\Delta H_f^\circ(\text{gas})$	72.2 kcal/mol
$\Delta G_f^\circ(\text{cry})(\text{white})$	0.0
$\Delta G_f^\circ(\text{cry})(\text{gray})$	0.03 kcal/mol
$\Delta G_f^\circ(\text{gas})$	63.9 kcal/mol
$S^\circ(\text{cry})(\text{white})$	12.32 cal/deg mol

$S^\circ(\text{cry})(\text{gray})$	10.55 cal/deg mol
$S^\circ(\text{gas})$	40.24 cal/deg mol
$C_p(\text{cry})(\text{white})$	6.45 cal/deg mol
$C_p(\text{cry})(\text{gray})$	6.16 cal/deg mol
$C_p(\text{gas})$	5.08 cal/deg mol
ΔH_{fus}	1.68 kcal/mol
Thermal conductivity(at 27°C)	0.666 W/cmK
Coefficient of linear expansion (at 25°C)	$22.0 \times 10^{-6}/^\circ\text{C}$

Production

Tin is produced commercially from mineral cassiterite, SnO_2 . The mineral is mined from alluvial sand deposits by different techniques, such as various dredging (usually applied to low-grade deposits), gravel-pump mining (on level ground), and open-pit mining. The ore is broken up mechanically by blasting and drilling. It then is crushed and ground to produce finely divided material that can be separated by gravity concentration and froth flotation. Tin concentrates so obtained require removal of sulfide before smelting. This is done by roasting concentrates at high temperatures which removes both sulfur and arsenic. Lead sulfide is converted to lead sulfate but all other associated metal sulfides, such as those of iron, copper, zinc, and bismuth, are converted to oxides.

Tin is produced from oxide by heating at high temperatures with carbon. Small amounts of limestone and sand are added to coal for this reduction and to promote removal of impurities. Primary smelting is carried out in a reverberatory furnace at a temperature between 1,200 to 1,300°C. Electric arc furnaces also are used. The molten tin collected at the bottom is cast into slabs. The slags are resmelted at a higher temperature, up to 1,480°, in the same type of furnaces to recover more tin that is combined as silicates.

Tin obtained above contains small amounts of impurities. It is purified by resmelting in a small reverberatory furnace at a temperature just above the melting point of tin. The molten tin is drawn out, separating iron, copper, arsenic, antimony, and other metals. Purified tin is further refined by boiling or polling processes to remove traces of impurity metals, such as lead and bismuth.

Reactions

At ordinary temperatures tin is stable in air. It actually forms a very thin protective oxide film. In powder form, and especially in the presence of moisture, it oxidizes. When heated with oxygen it forms tin(IV) oxide, SnO_2 . Tin reacts with all halogens forming their halides. Reaction with fluorine is slow at ordinary temperatures; however, chlorine, bromine and iodine readily react with the metal.

Tin is attacked by concentrated acids. With dilute acids the reaction may be slow or very slow. The metal readily reacts with hot concentrated hydrochloric acid and aqua regia but slowly with cold dilute hydrochloric acid. The reaction also is slow with hot dilute sulfuric acid, which dissolves the

metal, particularly in the presence of an oxidizing agent. The reaction with nitric acid is generally slow. Hot concentrated acid converts the metal to an insoluble hydrated tin(IV) oxide. The reaction is rapid with moist sulfur dioxide or sulfurous acid, chlorosulfonic, and pyrosulfuric acids. Organic acids such as, acetic, oxalic, and citric acids react slowly with the metal, particularly in the presence of air or an oxidizing agent.

Strong alkaline solutions of caustic soda or caustic potash dissolve tin forming the stannate, Na_2SnO_3 , or K_2SnO_3 . The metal is stable in dilute solutions of ammonia or sodium carbonate.

Tin dissolves in solutions of oxidizing salts such as potassium chlorate or potassium persulfate. The metal does not react with neutral salts in aqueous solutions. In air, tin reacts slowly with neutral salts.

The metal does not combine directly with hydrogen, nitrogen or ammonia gas.

Analysis

Tin can be measured readily at trace concentrations in aqueous solutions by flame or furnace atomic absorption spectrophotometry. For flame AA measurement, air-acetylene flame is suitable. The metal can be identified accurately at 224.6 nm. Tin also can be measured by other instrumental techniques such as ICP-AES, ICP/MS and neutron activation analysis.

TIN(II) CHLORIDE

[7772-99-8]

Formula: SnCl_2 ; MW 189.62; forms a dihydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ [10025-69-1], MW 225.65

Synonyms: stannous chloride; tin dichloride; tin protochloride

Uses

Tin (II) chloride is a strong reducing agent and is used in many industrial processes, such as manufacturing dyes, phosphors, and polymers. The compound is a major ingredient in acid tin plating baths. Other uses are a mordant in dyeing; an additive to lubricating oil to prevent sludging; a stabilizer for perfume in soaps; in removing ink stains; a sensitizing agent for glass, paper, and plastics; and a soldering flux. Tin(II) chloride is used for preparing a number of tin(II) salts. It is a catalyst in many organic reactions. It is a common laboratory reagent.

Physical Properties

White orthogonal crystal; density 3.90 g/cm³; melts at 247°C; vaporizes at 623°C; vapor pressure 1 torr at 316°C, 5 torr at 366°C and 20 torr at 420°C; soluble in water, ethanol, acetone and ether; insoluble in xylene and mineral spirits.

The dihydrate, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, is a white monoclinic crystalline substance; density 2.71 g/cm^3 ; absorbs oxygen from air forming an oxychloride; melts at 37°C on rapid heating; decomposes on strong heating; very soluble in water; forms an insoluble basic salt with excess water; very soluble in hydrochloric acid; soluble in caustic soda solution, ethanol and ethyl acetate.

Thermochemical Properties

ΔH_f°	-77.7 kcal/mol
ΔH_{fus}	3.06 kcal/mol
ΔH_{vap}	20.7 kcal/mol

Preparation

Tin(II) chloride is prepared by dissolving tin in hydrochloric acid followed by evaporation of the solution and crystallization.

Analysis

Elemental composition: Sn 62.60%, Cl 37.40%. An aqueous solution is analyzed to measure tin content. Chloride ion can be measured by ion chromatography or by chloride ion-selective electrode. Also, as a strong reducing agent, concentration of Sn^{2+} ion in an aqueous solution can be measured by redox titration.

TIN(IV) CHLORIDE

[7646-78-8]

Formula: SnCl_4 ; MW 260.52; forms a pentahydrate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ [10026-06-9], MW 350.60

Synonyms: stanic chloride; tin tetrachloride; tin perchloride

Uses

Tin(IV) chloride is a mordant for dyeing fabrics; a stabilizer for perfume in soap; used in weighting silk; in ceramic coatings; in manufacturing blue print papers; and to produce fuchsin. Also, tin(IV) chloride is used in preparing many organotin compounds.

Physical Properties

Colorless fuming liquid; corrosive; density 2.234 g/mL ; freezes at -33°C ; boils at 114.15°C ; critical temperature 318.75°C ; critical pressure 37.98 atm ; critical volume $351 \text{ cm}^3/\text{mol}$; soluble in cold water, evolving heat; decomposed by hot water; soluble in alcohol, benzene, toluene, chloroform, acetone and kerosene

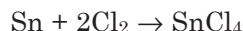
The pentahydrate is a yellowish-white crystalline solid or small, fused lumps; faint odor of HCl ; density 2.04 g/cm^3 ; decomposes at 56°C ; very soluble in water; soluble in ethanol

Thermochemical Properties

ΔH_f° (liq)	-122.2 kcal/mol
ΔH_f° (gas)	-112.7 kcal/mol
ΔG_f° (liq)	-105.2 kcal/mol
ΔG_f° (gas)	-103.3 kcal/mol
S° (liq)	61.8 cal/deg mol
S° (gas)	87.4 cal/deg mol
C_p (liq)	39.5 cal/deg mol
C_p (gas)	23.5 cal/deg mol
ΔH_{fus}	2.20 kcal/mol
ΔH_{vap}	8.34 kcal/mol

Preparation

Tin(IV) chloride is prepared by reacting tin or tin(II) chloride with chlorine:

**Analysis**

Elemental composition: Sn 45.56%, Cl 54.44%. The compound may be identified from its physical properties. An aqueous solution may be analyzed by AA, ICP and other techniques to determine tin content. The compound may be dissolved in toluene or carbon tetrachloride, diluted sufficiently, and analyzed by GC/MS.

TIN(II) OXIDE

[21651-19-4]

Formula: SnO ; MW 134.71

Synonyms: stannous oxide; tin monoxide; tin protoxide

Uses

Tin(II) oxide is a reducing agent; and is used in preparing other tin(II) salts. Also, it is used to make soft abrasive putty powder.

Physical Properties

Bluish-black powder; tetragonal crystals; density 6.45 g/cm³; decomposes at 1,080°C; insoluble in water; dissolves in acids to form Sn^{2+} and in base to form stannite ion, $\text{Sn}(\text{OH})_3^-$.

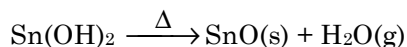
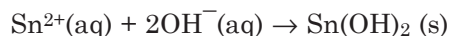
Thermochemical Properties

ΔH_f° (cry)	-67.1 kcal/mol
ΔH_f° (gas)	3.61 kcal/mol

ΔG_f° (cry)	-60.2 kcal/mol
ΔG_f° (gas)	-2.01 kcal/mol
S° (cry)	13.7 cal/deg mol
S° (gas)	55.5 cal/deg mol
C_p (cry)	10.6 cal/deg mol
C_p (gas)	7.55 cal/deg mol

Preparation

Tin(II) oxide is prepared by heating tin(II) hydroxide. The latter is obtained as a white precipitate by reacting Sn^{2+} ions with hydroxide ions:

**Analysis**

Elemental composition: Sn 88.12%, O 11.88%. Tin oxide is dissolved in nitric acid, diluted, and analyzed for tin (See Tin).

TIN(IV) OXIDE

[18282-10-5]

Formula: SnO_2 ; MW 150.71

Synonyms: stannic oxide; tin dioxide; tin peroxide; white tin oxide; stannic anhydride; flowers of tin

Occurrence and Uses

Tin(IV) oxide occurs in nature as mineral cassiterite. It is used to make specialty glasses, in manufacturing enamels and pottery, for polishing glass marbles, metals and decorative stones, as a mordant in dyeing and printing textiles, in perfumes, and nail polishes.

Physical Properties

White or grayish powder; tetragonal crystals; density 6.85 g/cm^3 ; refractive index 2.006; Mohs hardness 6.5; melts at $1,630^\circ\text{C}$; insoluble in water; soluble in hot concentrated alkalis

Thermochemical Properties

ΔH_f°	-138.0 kcal/mol
ΔG_f°	-123.3 kcal/mol
S°	11.7 cal/deg mol
C_p	12.6 cal/deg mol

Production

Tin(IV) oxide is mined from naturally-occurring cassiterite. Various techniques are employed in mining (See Tin). The ore is crushed, ground, and separated by gravity concentration and froth flotation. Sulfide impurities are removed by roasting the ore concentrates at high temperatures.

Tin(IV) oxide is prepared by precipitation from tin(IV) chloride solution by adding ammonium hydroxide. The overall reaction is:



The precipitate is washed with hot water.

Analysis

Elemental composition: Sn 78.77%, O 21.23%. Tin(IV) oxide can be identified by physical properties and x-ray diffraction. Tin content may be determined by various instrumental techniques in an acid solution of the oxide (See Tin). The compound is solubilized by digestion with nitric acid or aqua regia and diluted appropriately.

TIN(IV) SULFATE

[7488-55-77]

Formula: SnSO_4 ; MW 214.77

Synonyms: stannous sulfate; tin sulfate

Uses

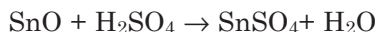
Tin(II) sulfate is used for electroplating automobile pistons and in other tin plating. Also, the compound is a mordant for dyeing; and is used in preparing tin(II) salts.

Physical Properties

Heavy white crystals; orthorhombic structure; density 4.15 g/cm³; decomposes at 378°C to SnO_2 and SO_2 ; soluble in water, reacting to form a basic sulfate that precipitates; soluble in dilute sulfuric acid.

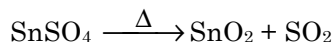
Preparation

Tin(II) sulfate is prepared by reacting tin(II) oxide with sulfuric acid:

**Analysis**

Elemental composition: Sn 55.27%, S 14.93%, O 29.80%. The compound is

dissolved in sulfuric acid, diluted, and analyzed for tin (See Tin). The compound is determined gravimetrically by decomposing at 378°C. The SO₂ gas produced is analyzed by GC/MS or by colorimetry (See Sulfur Dioxide) and the residue SnO₂ is analysed by gravimetry:



TITANIUM

[7440-32-6]

Symbol Ti; atomic number 22; atomic weight 47.867; a Group IVB (Group 4) transition metal; electron configuration [Ar]3d²4s²; valence +2, +3, +4; atomic radius 1.47Å; ionic radius, Ti³⁺ 0.67 Å and Ti⁴⁺ 0.61Å, respectively, corresponding to CN 6; standard electrode potential, E° for Ti²⁺ + 2e⁻ ↔ Ti is -1.63 V and Ti³⁺ + 3e⁻ ↔ Ti is -1.37 V; five naturally-occurring stable isotopes: Ti-46 (8.25%), Ti-47 (7.44%), Ti-48 (73.72%), Ti-49 (5.41%), Ti-50 (5.18%); fifteen artificial radioisotopes in the mass range 39-45, 51-58, the longest-lived isotope, Ti-44, t_{1/2} 67 years.

History, Occurrence and Uses

Titanium was discovered in 1790 by English chemist William Gregor. Five years later in 1795, Klaproth confirmed Gregor's findings from his independent investigation and named the element titanium after the Latin name *Titans*, the mythical first sons of the Earth. The metal was prepared in impure form first by Nilson and Pettersson in 1887. Hunter, in 1910, prepared the metal in pure form by reducing titanium tetrachloride with sodium.

Titanium occurs in nature in the minerals rutile (TiO₂), ilmenite (FeTiO₃), geikielite, (MgTiO₃) perovskite (CaTiO₃) and titanite or sphene (CaTiSiO₄(O,OH,F)). It also is found in many iron ores. Abundance of titanium in the earth's crust is 0.565%. Titanium has been detected in moon rocks and meteorites. Titanium oxide has been detected in the spectra of M-type stars and interstellar space.

Titanium is found in plants, animals, eggs, and milk.

Many titanium alloys have wide industrial applications. Titanium forms alloys with a number of metals including iron, aluminum, manganese, and molybdenum. Its alloys are of high tensile strength, lightweight, and can withstand extreme temperatures. They are used in aircraft and missiles. The metal also has high resistance to sea water corrosion and is used to protect parts of the ships exposed to salt water. Also, titanium is used to combine with and remove traces of oxygen and nitrogen from incandescent lamps. Titanium

compounds, notably the dioxide and the tetrachloride, have many uses (See Titanium Dioxide and Titanium Tetrachloride.)

Physical Properties

White lustrous metal; ductile when free of oxygen; low density high strength metal.

Titanium has two allotropic modifications: (1) alpha form and (2) beta modification. The alpha form has a close-packed hexagonal crystal structure; density 4.54 g/cm³ at 20°C and stable up to 882°C. It converts very slowly to a body-centered cubic beta form at 882°C. The density of the beta form is 4.40 g/cm³ at 900°C (estimated). The other physical properties are as follows:

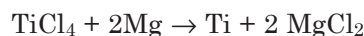
The metal melts at 1,610 ±10°C; vaporizes at 3,287°C; electrical resistivity 42 microhm-cm; modulus of elasticity 15.5x10⁶ psi at 25°C; tensile strength, ultimate 34,000 psi (at 25°C); tensile strength yield 20,000 psi (at 25°C); Vickers hardness 80-100; surface tension at the melting point 1427 dynes/cm³; superconductivity below 1.73°K; thermal neutron absorption cross section 5.8 barns; insoluble in water; soluble in dilute acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	112.3 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	101.6 kcal/mol
S° (cry)	7.32 cal/deg mol
S° (gas)	43.1 cal/deg mol
C_p (cry)	5.98 cal/deg mol
C_p (gas)	5.84 cal/deg mol
ΔH_{fus}	3.38 kcal/mol
Thermal conductivity(at 27°C)	0.219 W/cm K
Coefficient of linear expansion (at 25°C)	8.6x10 ⁻⁶ /°C

Production

The production of titanium always encounters difficulties because of a tendency to react with oxygen, nitrogen and moisture at elevated temperatures. Most high purity elemental titanium can be produced by the Kroll process from titanium tetrachloride. The tetrachloride is reduced with magnesium in a mild steel vessel at about 800°C under an inert atmosphere of helium or argon. The net reaction is as follows:



The reaction is highly exothermic providing heat needed to maintain high temperature required for reaction. The Kroll process is applied commercially to produce elemental titanium.

Sodium metal can be used instead of magnesium in thermally reducing titanium tetrachloride.

Titanium metal also can be produced by electrolytic methods. In electrolysis, fused mixtures of titanium tetrachloride or lower chlorides with alkaline earth metal chlorides are electrolyzed to produce metal. Also, pure titanium can be prepared from electrolysis of titanium dioxide in a fused bath of calcium-, magnesium- or alkali metal fluorides. Other alkali or alkaline metal salts can be substituted for halides in these fused baths. Other titanium compounds that have been employed successfully in electrolytic titanium production include sodium fluotitanate and potassium fluotitanate.

Very highly pure titanium metal can be prepared in small amounts by decomposition of pure titanium tetraiodide, (TiI₄) vapor on a hot wire under low pressure (Van Arkel–de Boer method).

Reactions

Titanium metal is very highly resistant to corrosion. It is unaffected by atmospheric air, moisture and sea water, allowing many of its industrial applications. The metal burns in air at about 1,200°C incandescently forming titanium dioxide TiO₂. The metal also burns on contact with liquid oxygen.

Titanium forms four oxides, all of which have been well described. It forms a weakly basic monoxide, TiO; a basic dititanium trioxide, Ti₂O₃; the amphoteric dioxide, TiO₂; and the acidic trioxide, TiO₃.

Titanium combines with nitrogen at about 800°C forming the nitride and producing heat and light. It is one of the few elements that burns in nitrogen.

Titanium reacts with all halogens at high temperatures. It reacts with fluorine at 150°C forming titanium tetrafluoride, TiF₄. Reaction with chlorine occurs at 300°C giving tetrachloride TiCl₄. Bromine and iodine combine with the metal at 360°C forming their tetrahalides.

Water does not react with Ti metal at ambient temperatures, but titanium reacts with steam at 700°C forming the oxide and hydrogen:



Titanium is soluble in hot concentrated sulfuric acid, forming sulfate. It also reacts with hydrofluoric acid forming the fluoride.

Nitric acid at ordinary temperatures does not react with Ti metal, but hot concentrated nitric acid oxidizes titanium to titanium dioxide.

The metal is stable with alkalis.

Titanium combines with several metals, such as, iron, copper, aluminum, chromium, cobalt, nickel, lead and tin at elevated temperatures forming alloys.

Analysis

Titanium can be measured at trace concentrations by flame-AA using a nitrous oxide-acetylene flame. The measurement can be done at 365.3 nm. ICP-AES and ICP/MS techniques also are applicable. The metal or its compounds must be dissolved by digestion with HF and HCl and the solution diluted and analyzed instrumentally.

TITANIUM DIOXIDE

[13463-67-7]

Formula: TiO_2 ; MW 79.866

Synonyms: titanic oxide; titanic acid anhydride; titanium anhydride; titania; titanium white

Uses

Titanium dioxide is an extreme white and bright compound with high index of refraction. In paints it is a white pigment and an opacifying agent. It is in house paints, water paints, lacquers, enamels, paper filling and coating, rubber, plastics, printing ink, synthetic fabrics, floor coverings, and shoe whiteners. Also, it is used in colorants for ceramics and coatings for welding rods. A rutile form of the dioxide is used in synthetic gem stones.

Physical Properties

The naturally occurring dioxide exists in three crystal forms: anatase, rutile and brookite. While rutile, the most common form, has an octahedral structure. Anatase and brookite have very distorted octahedra of oxygen atoms surrounding each titanium atom. In such distorted octahedral structures, two oxygen atoms are relatively closer to titanium than the other four oxygen atoms. Anatase is more stable than the rutile form by about 8 to 12 kJ/mol (Cotton, F.A., Wilkinson, G., Murillo, C.A and M Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed, p. 697, New York: John Wiley & Sons) Other physical properties are: density 4.23g/cm³; Mohs hardness 5.8 g/cm³ (anatase and brookite) and 6.2 g/cm³ (rutile); index of refraction 2.488 (anatase), 2.583 (brookite) and 2.609 (rutile); melts at 1,843°C; insoluble in water and dilute acids; soluble in concentrated acids.

Thermochemical Properties

ΔH_f°	-225.6 kcal/mol
ΔG_f°	-212.4 kcal/mol
S°	12.1 cal/deg mol
C_p	13.1 cal/deg mol

Production

Titanium dioxide is mined from natural deposits. It also is produced from other titanium minerals or prepared in the laboratory. Pigment-grade dioxide is produced from the minerals, rutile and ilmenite. Rutile is converted to pigment grade rutile by chlorination to give titanium tetrachloride, TiCl_4 . Anhydrous tetrachloride is converted back to purified rutile form by vapor phase oxidation.

Anatase form is obtained by hydrolytic precipitation of titanium(IV) sulfate on heating. The mineral ilmenite is treated with concentrated sulfuric acid. Heating the sulfate solution precipitates hydrous titanium oxide. The precipitate is calcined to expel all water.

Titanium dioxide also can be prepared by heating Ti metal in air or oxygen at elevated temperatures.

Analysis

Elemental composition: Ti 59.95%, O 40.05%. The oxide may be identified by its physical properties and by x-ray methods. Titanium content may be measured by AA or ICP. The compound is digested in nitric acid or aqua regia, solubilized, and diluted sufficiently for metal analysis.

TITANIUM HYDRIDE

[7704-98-5]

Formula: TiH_2 ; MW 49.883

Uses

Titanium dihydride is an additive in powder metallurgy. Other uses are producing foamed metals, making solder for metal-glass composites; a getter for oxygen and nitrogen in electronic tubes; a source of pure hydrogen; and a reducing agent.

Physical Properties

Grayish-black metallic powder; stable in air; density 3.75 g/cm³; decomposes at 450°C with evolution of hydrogen; insoluble in water

Production

Titanium hydride is prepared by heating titanium dioxide with calcium hydride at 600°C in the presence of hydrogen.

Also, the hydride may be prepared by heating titanium metal with hydrogen at elevated temperatures.

Analysis

Elemental composition: Ti 95.95%, H 4.04%. A measured amount of hydride is decomposed at about 450°C and the volume of liberated hydrogen is measured. The hydride is digested cautiously in aqua regia, diluted and analyzed for titanium.

Hazard

Violent reaction can occur in contact with a strong oxidizing agent.

TITANIUM TETRACHLORIDE

[7550-45-0]

Formula: TiCl_4 ; MW 189.68

Synonym: titanium(IV) chloride

Uses

Titanium tetrachloride is used to prepare titanium dioxide and most other titanium compounds. It also is used in making iridescent glass; artificial pearls; and smoke screens. The compound is a polymerization catalyst.

Physical Properties

Colorless or yellow liquid; penetrating acid odor; absorbs moisture from air; produces dense white fumes; density 1.73 g/mL; freezes at -25°C ; boils at 136.5°C ; critical temperature 464.8°C ; critical pressure 46.6 atm; critical volume $339\text{ cm}^3/\text{mol}$; reacts with water forming TiO_2 and HCl ; soluble in ethanol

Thermochemical Properties

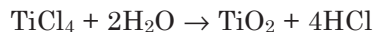
$\Delta H_f^\circ(\text{liq})$	-192.2 kcal/mol
$\Delta H_f^\circ(\text{gas})$	-182.4 kcal/mol
$\Delta G_f^\circ(\text{liq})$	-176.2 kcal/mol
$\Delta G_f^\circ(\text{gas})$	-173.6 kcal/mol
$S^\circ(\text{liq})$	60.3 cal/deg mol
$S^\circ(\text{gas})$	84.4 cal/deg mol
$C_p(\text{liq})$	34.7 cal/deg mol
$C_p(\text{gas})$	22.8 cal/deg mol
ΔH_{vap}	3.65 kcal/mol

Preparation

Titanium tetrachloride is prepared by heating titanium dioxide or the ores ilmenite or rutile with carbon to red heat in a stream of chlorine. When ilmenite is used, ferric chloride also is produced. Titanium tetrachloride is separated from ferric chloride and other impurities by fractionation.

Analysis

Elemental composition: Ti 25.25%, Cl 74.75%. The compound is digested in acid, diluted and analyzed for titanium (See Titanium). A small amount of compound is weighed accurately and decomposed in hot water to form TiO_2 and HCl :



The product HCl is measured by acid-base titration. An aliquot of the product mixture is analyzed for chloride ion by ion chromatography or titration with a standard solution of silver nitrate. The compound can be identified from its physical properties.

TITANIUM TRICHLORIDE

[7705-07-9]

Formula: TiCl_3 ; MW 154.22

Synonyms: titanous chloride; titanium(III) chloride

Uses

Titanium trichloride is a reducing agent. It is used to analyse nitro groups, ferric ion, perchlorate, and other oxidizing analytes. The trichloride also is a stripping agent for removing stains in laundering.

Physical Properties

Red-violet hexagonal crystals; hygroscopic; density 2.64 g/cm^3 ; decomposes on heating above 425°C ; also decomposes in water, evolving heat; soluble in alcohol, acetonitrile and certain amines; insoluble in hydrocarbons and ether

Thermochemical Properties

ΔH_f°	-172.3 kcal/mol
ΔG_f°	-156.2 kcal/mol
S°	33.4 cal/deg mol
C_p	23.2 cal/deg mol
ΔH_{vap}	29.6 kcal/mol

Preparation

Titanium trichloride may be prepared by reducing titanium tetrachloride with hydrogen at 600°C . The tetrachloride may alternatively be reduced with aluminum, zinc, magnesium, tin, or by electrolysis.

Analysis

Elemental composition: Ti 31.05%, Cl 68.95%. Because it is a strong reducing agent and its aqueous solution is stable, the trichloride can be measured by redox titration. Also, titanium can be analyzed by various instrumental methods after digestion in an acid.

TUNGSTEN

[7440-33-7]

Symbol W; atomic number 74; atomic weight 183.85; a Group IV B (Group 6) chromium-group transition metal element; electron configuration $[\text{Xe}]4f^{14}5d^46s^2$; valence 0, +2, +3, +4, +5, +6; atomic radius $1.39 \text{ \AA}$; ionic radius $0.66 \text{ \AA}$ and $0.62 \text{ \AA}$ for W^{4+} and $^{5+}$ corresponding to $\text{CN}6$ and $0.42 \text{ \AA}$ for W^{6+} at $\text{CN}4$; standard electrode potential, E° for $\text{W}^{3+} + 3e^- \leftrightarrow \text{W}$ is 0.10 V ; five naturally-occurring stable isotopes: W-180 (0.120%), W-182 (26.498%), W-183 (14.314%), W-184 (30.642%), W-186 (28.426%); twenty-eight artificial radioisotopes in the mass range 158–179, 181, 185, 187–190; longest-lived isotope, W-181 $t_{1/2}$ 121.2 days.

History, Occurrence and Uses

The discovery of tungsten occurred in the 1780's. Peter Woulfe, in 1779, while examining the mineral now known as wolframite, established that it contained a new substance. Around the same time, Swedish chemist Carl Wilhelm Scheele was investigating another mineral, scheelite. This mineral was known at that time as tungsens, which in Swedish meant heavy stone. Scheele, in 1781, determined that tungsens contained lime and a new acid similar to molybdic acid. This new acid was tungstic acid. Scheele and Bergman predicted that reduction of this acid could produce a new metal. Two years later in 1783, J. J. de Elhuyar and his brother F. de Elhuyar of Spain first prepared metallic tungsten from wolframite. They derived an acid from wolframite which was similar to acid obtained by Scheele from tungsten (scheelite), and succeeded in producing a new metal by reduction of this acid with charcoal. Also, they determined that the mineral wolframite contained iron and manganese. The metal took over the old name of its mineral tungsten. Also the metal is known as wolfram, derived from the name of its other mineral, wolframite. The word wolfram originated from the wolf-like nature of the mineral that it devoured tin during the tin smelting operation causing low recoveries. The element was given the symbol W for its old name wolfram.

Tungsten is widely distributed in nature, occurring in several minerals. It is found in scheelite, CaWO_4 ; wolframite, $(\text{Fe}, \text{Mn})\text{WO}_4$; huebnerite, MnWO_4 ; ferberite, FeWO_4 ; tungstite, H_2WO_4 ; and cuprotungstite, CuWO_4 . Its abundance in the earth's crust is estimated to be 1.25 mg/kg and average concentration in seawater is about 0.1 $\mu\text{g/L}$.

Industrially tungsten is a very important metal having wide applications. This is due to many outstanding physical properties. Among all the metals, tungsten has the highest melting point and the lowest vapor pressure. Also at high temperatures it has the highest tensile strength. The metal has an excellent resistance to corrosion and attack by mineral acids. Also it has a thermal expansion comparable to that of borosilicate glass.

Tungsten is extensively used in alloy steel to impart high strength and hardness to steel. Heavy metal alloys with nickel, copper and iron, produced by powder metallurgy, can be made machineable and moderately ductile for applications as high-density materials. Tungsten carbides are extremely hard and are excellent cutting materials. They are used extensively in the tool and die industry for drilling and cutting tools, sand blasting nozzels, armor-piercing bullets, and studs to increase traction of tires.

Among the nonferrous tungsten alloys, its alloys with copper and silver are used as electrical contacts and switches and with molybdenum in aerospace components.

Unalloyed tungsten has several major applications. An important use is in the electric lamp filaments for light bulbs. Also, it is used as electrodes in arc-welding, in heating elements for high-temperature furnaces, in electron and television tubes, in glass-to-metal seals, and in solar energy devices.

Physical Properties

Grayish-white metal; body-centered cubic crystalline structure; density 19.3 g/cm³; melts at 3,422°C; vaporizes at 5,555°C; vapor pressure 1 torr at 3,990°C; electrical resistivity 5.5 microhm-cm at 20°C; modulus of elasticity about 50 to 57 × 10⁶ psi (single crystal); Poisson's ratio 0.17; magnetic susceptibility +59 × 10⁻⁶; thermal neutron absorption cross section 19.2 ± 1.0 barns (2,200m/sec); velocity of sound, about 13,000 ft/sec; insoluble in water; practically insoluble in most acids and alkalies; dissolves slowly in hot concentrated nitric acid; dissolves in saturated aqueous solution of sodium chlorate and basic solution of potassium ferricyanide; also solubilized by fusion with sodium hydroxide or sodium carbonate in the presence of potassium nitrate followed by treatment with water

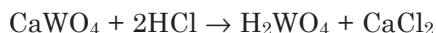
Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	203.0 kcal/mol
$\Delta G_f^\circ(\text{gas})$	192.9 kcal/mol
$S^\circ(\text{cry})$	7.79 cal/deg mol
$S^\circ(\text{gas})$	41.6 cal/deg mol
$C_p(\text{cry})$	5.81 cal/deg mol
$C_p(\text{gas})$	5.09 cal/deg mol
ΔH_{fus}	12.5 kcal/mol
Thermal conductivity	1.74 W/cmK
Coefficient of linear expansion	4.5 × 10 ⁻⁶ /°C

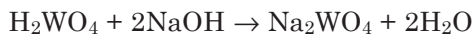
Production

Tungsten is recovered mostly from mineral scheelite and wolframite. The recovery process depends on the mineral, the cost, and the end use; i.e., the commercial products to be made. Typical industrial processes have been developed to convert tungsten ores to tungsten metal and alloy products, tungsten steel, non-ferrous alloys, cast and cemented tungsten carbides, and tungsten compounds. A few processes are mentioned briefly below.

The first step in recovery is opening the ore. If the ore is scheelite, CaWO₄, it is digested with hydrochloric acid:



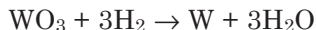
Tungstic acid, H₂WO₄ precipitates out. The precipitate is washed and dissolved in sodium or ammonium hydroxide solution during heating:



Sodium tungstate is crystallized, separated from any impurities in the solution, and digested again with hydrochloric acid to form tungstic acid in purified form. The pure acid is dried, ignited and reduced with carbon to form tungsten powder from which most non-ferrous alloys are made.

The tungstic acid may be dissolved in ammonium hydroxide solution

instead of sodium hydroxide and evaporated to form ammonium paratungstate (APT) crystals, $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$. The APT crystals are washed, dried and calcined to obtain tungstic oxide, WO_3 . The latter then is reduced with hydrogen at $1,100^\circ\text{C}$ to form tungsten powder:



The APT may directly be reduced with hydrogen to produce tungsten powder. The powder may be pressed, sintered and fabricated to produce tungsten metal and alloy products. The tungsten powder may be heated with carbon to form tungsten carbides which may be converted to cast carbides or certain grades of cemented carbides. Or the tungsten powder may be alloyed with specific metals to form various non-ferrous alloys.

If tungsten is recovered from the wolframite group mineral, the wolframite concentrate is boiled or pressure-digested with 50% caustic soda solution. Alternatively, they may be fused or sintered with caustic soda, caustic potash or sodium carbonate and the fused mass then leached with water. The solution is filtered to separate sodium tungstate solution. The filtrate is subjected to various treatments to remove molybdenum, phosphorus, and arsenic impurities. The filtrate at this point is essentially a solution of sodium tungstate and is treated in the same way as that obtained from the scheelite concentrate discussed above.

Commercial ferrotungsten is obtained by reducing wolframite, scheelite, ferberite or hybnerite with carbon in an electric furnace. Iron scrap is added in appropriate amounts to form a ferrotungsten alloy containing about 70 to 80% tungsten.

Reactions

Tungsten exhibits several oxidation states, +6 being most stable. Compounds of lower oxidation states show alkaline properties. They also are less stable than those produced in higher oxidation states. Tungsten exhibits remarkable stability to practically all substances at ambient temperature. The metal is not attacked by nonoxidizing mineral acid. Concentrated hydrochloric acid, dilute sulfuric acid and hydrofluoric acid attack the metal very slightly even when heated to 100°C . Tungsten is stable to dilute or concentrated nitric acid under cold conditions. Cold acid passivates the surface forming a slight oxide film. Hot dilute nitric acid corrodes the metal, while hot concentrated acid slowly dissolves bulk metal but rapidly oxidizes metal in powder form. At room temperature, aqua regia oxidizes metal only on the surface forming tungsten trioxide. A hydrofluoric-nitric acid mixture rapidly oxidizes tungsten to its trioxide. Chromic acid-sulfuric acid mixture does not react with tungsten metal in ductile form at ambient temperatures.

Tungsten metal is not affected by aqueous alkalis at room temperature. In molten state, caustic soda and caustic potash slowly oxidize tungsten in the presence of air. Oxidation is more rapid in the presence of an oxidizing agent such as potassium nitrate, potassium chlorate, or lead dioxide. A similar reaction occurs with fused sodium or potassium carbonate. Tungsten dissolves

slowly in molten salt but when an oxidizing agent is added to molten carbonate mixture, the reaction speeds up.

Although tungsten exhibits a high degree of resistance to most chemicals, it is readily oxidized by a number of oxidizing agents. A 30% solution of hydrogen peroxide dissolves metal powder slowly at room temperature. A similar reaction happens in a saturated solution of sodium or potassium chlorate.

Tungsten reacts with oxygen at high temperatures. The finely-divided powder is pyrophoric. But the bulk metal begins to oxidize at about 400°C. The metal oxidizes rapidly when heated in air or oxygen at red heat. Two simple oxides are known, a blue monoclinic dioxide, WO_2 , and a lemon yellow trioxide, WO_3 . The trioxide, WO_3 , is the most stable oxide and the ultimate product of heating the metal in oxygen. Many other oxides also are known, but they are of nonstoichiometric compositions and are unstable. The metal also is oxidized by water vapor at red heat.

Tungsten reacts with all halogens. With fluorine, reaction occurs at room temperature forming a volatile hexafluoride, WF_6 . Pure dry chlorine gas combines with the metal above 250°C to form purple tungsten hexachloride, WCl_6 . In the presence of moisture, oxychlorides (or tungstic oxides) are formed. Tungsten reacts with bromine vapor at red heat forming brownish-black pentabromide, WBr_5 . The metal reacts with iodine vapor at red heat to form black tetraiodide, WI_4 . At a lower temperature of about 730°C, the product is orange diiodide, WI_2 .

Tungsten reacts with ammonia at elevated temperatures forming tungstic nitrides and amides. Tungsten ordinarily does not combine with nitrogen. At very high temperatures above 1,500°C nitrides, WN_2 and W_2N , are produced. These nitrides also are prepared at lower temperatures by reacting ammonia with tungsten powder.

Tungsten reacts with molten sulfur forming the disulfide, WS_2 . In excess sulfur the trisulfide, WS_3 forms.

Tungsten forms a volating white crystalline hexacarbonyl, $\text{W}(\text{CO})_6$ by reacting with carbon monoxide at 275 to 300°C under 200 atm CO pressure.

Tungsten forms a number of compounds with nonmetals and light metalloid elements. Many are important refractory materials in commerce. The most important are the carbides, WC and W_2C . They are made by heating tungsten and carbon together at about 1,500°C. The carbide, WC , in powder form is made by heating a mixture of tungsten powder and finely divided lamp black in hydrogen at about 1,500°C. Carbide for commercial uses is produced by ball milling with about 5 to 30% binder, such as cobalt. The mixture then is pressed, preheated at about 900°C in hydrogen, machined to final shape and sintered at about 1,300 to 1,400°C. Cast carbides are made by melting a mixture of tungsten powder (reduced by carbon) and a carbonaceous material at 3,000 to 3,200°C.

Tungsten also forms hard, crystalline refractory borides, such as WB_2 , W_2B and WB when heated with boron in an electric furnace. Tungsten also forms a group of silicides, hard refractory compounds of compositions WSi_2 , WSi_3 and W_2Si_3 . These silicides are attacked by hydrofluoric-nitric acid mixture or by fused alkalis.

Analysis

Tungsten may be analyzed by flame AA and ICP-AES. For such analyses, the metal, its compounds, or alloys are solubilized by digestion with aqua regia, nitric acid-perchloric acid, or other acid combinations and diluted. Other instrumental techniques such as x-ray fluorescence and neutron activation analysis also are applicable.

TUNGSTEN HEXACARBONYL

[14040-11-0]

Formula: $\text{W}(\text{CO})_6$; MW 351.90

Synonym: tungsten carbonyl

Uses

Tungsten hexacarbonyl is used to produce tungsten coatings on base metals. This is done by deposition of the carbonyl on the metal surface, which decomposes to leave a tungsten coating.

Physical Properties

White crystalline solid; density 2.65 g/cm³; decomposes at 170°C without melting; sublimes; vapor pressure 0.1 torr at 20°C; insoluble in water; soluble in most organic solvents.

Preparation

Tungsten hexacarbonyl is produced by heating tungsten metal with carbon monoxide at high pressure. Also, carbonyl can be prepared by reducing the tungsten hexachloride by heating with iron powder under carbon monoxide pressure.

Analysis

Tungsten carbonyl may be dissolved in an organic solvent and analyzed by GC/MS. The compound should form mass spectra corresponding to the masses for $\text{W}(\text{CO})_6$, CO and W. The compound may be decomposed thermally and product carbon monoxide transported with helium onto a GC column to be analyzed by GC-TCD or GC/MS. Residue tungsten metal is extracted with nitric acid-hydrofluoric acid, diluted with water, and analyzed (See Tungsten).

TUNGSTEN TRIOXIDE

[1314-35-8]

Formula: WO_3 ; MW 231.84

Synonyms: tungsten(VI) oxide; tungstic oxide; tungstic acid anhydride;

tungstic anhydride; wolframic acid, anhydrous

Uses

Tungsten trioxide is used for fireproofing fabrics and as a yellow pigment in ceramics. It is used to make tungstates for x-ray screens. Also, it serves as starting material for preparing many tungsten compounds and tungsten metal.

Physical Properties

Heavy yellow powder; turns dark orange on heating; reverts back to yellow on cooling; density 7.2 g/cm³; melts at 1,472°C; insoluble in water; slightly soluble in acids; soluble in caustic alkalies

Thermochemical Properties

ΔH_f°	-201.5 kcal/mol
ΔG_f°	-182.6 kcal/mol
S°	18.1 cal/deg mol
C_p	17.6 cal/deg mol

Preparation

Tungsten trioxide is obtained as an intermediate in recovery of tungsten from its minerals (See Tungsten). In commercial processes tungstic acid, H₂WO₄, obtained from the mineral scheelite, may either be decomposed at high temperatures to form trioxide or dissolved in ammonium hydroxide solution and evaporated to yield ammonium paratungstate (APT) crystals, 5 (NH₄)₂O · 12WO₃ · 11H₂O. The APT crystals are then washed, dried, and calcined at elevated temperatures to form tungsten trioxide.

Tungsten trioxide, in general, can be made by heating metallic tungsten, its carbides, its lower oxides, or tungstic acid in air.

Analysis

Elemental composition: W 79.30%, O 20.70%. Tungsten trioxide may be identified by its physical properties or by x-ray diffraction methods. The oxide is either digested in aqua regia or dissolved in caustic alkalies, diluted, and analyzed for tungsten metal (See Tungsten).

TUNGSTIC ACID

[7783-03-1]

Formula: H₂WO₄; MW 249.85

Synonyms: orthotungstic acid; tungstic(VI) acid

Uses

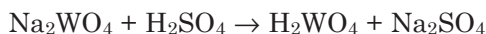
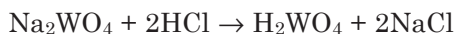
Tungstic acid is used in preparing tungsten metal and many tungsten compounds. Also, it is a mordant for textiles.

Physical Properties

Yellow amorphous powder; density 5.59 g/cm³; decomposes at 100°C; insoluble in water and most acids; soluble in hydrofluoric acid, caustic alkalies and ammonia solution. Freshly prepared tungstic acid containing a molecule of water of crystallization is moderately soluble in water.

Preparation

Tungstic acid is obtained as an intermediate in the recovery of tungsten from its minerals, scheelite and wolframite (See Tungsten). Also, the tungstic acid may be prepared by heating sodium tungstate with sulfuric acid or hydrochloric acid:



Analysis

Elemental composition: W 73.59%, H 0.81%, O 25.61%. The compound is dissolved in hydrofluoric acid and the solution diluted with water and analyzed for tungsten (See Tungsten).

URANIUM

[7440-61-4]

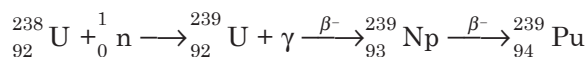
Symbol U; atomic number 92; atomic weight 238.029; an actinide series radioactive element; heaviest naturally-occurring element; electron configuration [Rn]5f³6d¹7s²; valence states +2, +3, +4, +5, +6; ionic radii U³⁺ 1.03 Å, U⁴⁺ 0.89 Å, U⁵⁺ 0.76 Å, for coordination number 6 and U⁶⁺ 0.45 Å and 0.81 Å for coordination numbers 2 and 7, respectively; standard electrode potential, E° for U³⁺ + 3e⁻ ↔ U is -1.798V and U⁴⁺ + e⁻ ↔ U³⁺ is -0.607V; twenty-two isotopes in the mass range 218–219, 222–240, 242; all isotopes are radioactive; Longest-lived isotope U-238, t_{1/2} 4.46x10⁹ years.

History, Occurrence and Uses

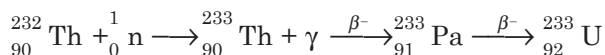
The element was discovered in the pitchblende ores by the German chemist M.S. Klaproth in 1789. He named this new element uranium after the planet Uranus which had just been discovered eight years earlier in 1781. The metal was isolated first in 1841 by Peligot by reducing the anhydrous chloride with potassium. Its radioactivity was discovered by Henry Becquerel in 1896. Then in the 1930's and 40's there were several revolutionary discoveries of nuclear properties of uranium. In 1934, Enrico Fermi and co-workers observed the beta radioactivity of uranium, following neutron bombardment and in 1939, Lise Meitner, Otto Hahn, and Fritz Strassmann discovered fission of uranium nucleus when bombarded with thermal neutrons to produce radioactive iso-

topes of lighter elements. Shortly after this, it was proved that only uranium-235 was fissionable while nonfissionable uranium-238 could be transmuted to a synthetic element, plutonium, by neutron irradiation. Plutonium also was fissionable by thermal neutrons like uranium-235. Fermi and his co-workers first successfully carried out a self-sustaining chain reaction in 1942. These investigations led to the first test of a nuclear explosive device in New Mexico in July 1945. This was followed by the first explosion of a nuclear bomb in Hiroshima, Japan in August 1945.

Uranium-235 is the most important uranium isotope for nuclear fuel. Uranium-238, although not fissionable itself, can be converted into the fissionable plutonium-239 in a breeder reactor by the following nuclear reaction:



Uranium-233, like uranium-235 and plutonium-239, forms a fissionable isotope used as nuclear fuel. This isotope can be made from natural thorium by irradiation with neutrons, as follows:



Uranium occurs in nature in many rocks, minerals and sediments. The principal uranium minerals are pitchblende, carnotite, uraninite, tobernite, uranophane, autunite, and davidite. Uranium also is found in very small quantities in monazite sand, phosphate rock, and lignite. Although uranium is present in very small quantities, these sources also are used for commercial recovery of the metal.

Abundance of uranium in the earth's crust is about 2.7 mg/kg. Its average concentration in seawater is 3.2 µg/L. The principal application of uranium is as nuclear fuel for reactors to generate electric power and to make nuclear explosives. Other uses are for making artificial elements, x-ray targets for producing high-energy x-rays, and in inertial guidance devices. Uranium salts are used in making yellow vaseline glass and glazes.

Physical Properties

Silvery-white heavy metal; malleable and ductile; slightly paramagnetic; density 18.95 g/cm³

The metal exists in three crystal forms: an orthorhombic alpha phase, density 18.97 g/cm³ and stable to 667°C; a tetragonal beta phase of density 18.11 g/cm³, stable between 688 to 776°C; and a body-centered cubic form of density 18.06 g/cm³ and stable in the range 776 to 1,132°C. Other physical properties are listed below:

The metal melts at 1,132°C; vaporizes at 4,131°C; electrical resistivity 28 microhm-cm; specific activity of total uranium (including the isotopes 238, 235 and 233) 1,501 disintegration/minute/mg; insoluble in water and alkalies; soluble in acids.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	127.4 kcal/mol
$\Delta G_f^\circ(\text{gas})$	116.7 kcal/mol
$S^\circ(\text{cry})$	12.0 cal/deg mol
$S^\circ(\text{gas})$	47.8 cal/deg mol
$C_p(\text{cry})$	6.62 cal/deg mol
$C_p(\text{gas})$	5.66 cal/deg mol
ΔH_{vap}	2.18 kcal/mol
Thermal conductivity(at 27°C)	0.276 W/cm K
Coefficient of linear expansion (at 25°C)	$13.9 \times 10^{-6}/^\circ\text{C}$

Recovery

The ore is crushed and finely ground. Uranium in the ore is concentrated by leaching with either an acid or an alkali. Uranium as oxide, U_3O_8 , is recovered from this leachate by ion exchange, solvent extraction or precipitation. The oxide is dissolved in concentrated nitric acid to form a solution of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$. The uranyl nitrate is separated from associated impurities by solvent extraction using tributyl phosphate. Heating uranyl nitrate with hydrogen at elevated temperatures converts it to the oxide, UO_2 . The oxide may be converted to uranium tetrafluoride, UF_4 , upon heating with hydrogen fluoride.

Metallic uranium can be prepared from its oxides or halides by reduction at high temperature. Uranium dioxide, UO_2 , or other oxides such as UO_3 or U_3O_8 may be reduced to uranium metal by heating with carbon, calcium or aluminum at high temperatures. Similarly, uranium tetrafluoride or other halides can be reduced to metal by heating with sodium, potassium, calcium, or magnesium at high temperatures. Alternatively, uranium tetrafluoride mixed with fused alkali chlorides is electrolyzed to generate uranium metal.

Reactions

In aqueous solution, uranium exists in four oxidation states: U^{3+} (red), U^{4+} (green) and its oxide ion UO_2^+ which is unstable, and the yellow uranyl ion, UO_2^{2+} . In solid compounds the metal exhibits several oxidation states.

Uranium forms several oxides. The main oxides are brown-black UO_2 , orange yellow UO_3 , and nonstoichiometric greenish black U_3O_8 . The most stable oxide is dioxide, UO_2 . Heating the metal in air or oxygen at 150 to 350°C forms UO_2 and U_3O_8 . A trihydride, UH_3 , is obtained when metal is heated in hydrogen at 250°C.

Uranium forms two stable fluorides, UF_4 and UF_6 . When metal is heated with fluorine gas, hexafluoride, UF_6 , is produced. Heating powdered metal with hydrogen fluoride gas at 350°C yields tetrafluoride, UF_4 . Powdered metal is obtained by thermal decomposition of trihydride, UH_3 . Uranium combines with chlorine at elevated temperature (at about 500°C) to form a mixture of various chlorides; namely, the tetrachloride, UCl_4 , pentachloride, UCl_5 , and hexachloride, UCl_6 . Heating the metal with bromine vapor at 650°C forms tetrabromide, UBr_4 . Uranium also forms tri- and pentabromides. With

iodine vapor at 350°C, products are the triiodide, UI_3 , and tetraiodide, UI_4 .

Uranium forms three stable and well-known sulfides, US , US_2 and U_2S_3 . While heating the metal with molten sulfur at 500°C forms the disulfide, US_2 , all the three sulfides are obtained from reacting hydrogen sulfide with the metal, particularly in its powder form at 500°C.

Heating the metal with ammonia at elevated temperatures (at about 700°C) yields nitrides of nonstoichiometric compositions. With nitric oxide, uranium is oxidized at about 400°C, forming triuranium octaoxide, U_3O_8 .

Both carbon monoxide and carbon dioxide oxidize uranium at 750°C forming uranium dioxide, UO_2 , along with uranium carbide, UC .

The same carbide is produced by heating the powdered metal with methane at elevated temperatures. Uranium forms mono- and dicarbides and diuranium tricarbides, UC , UC_2 , and U_2C_3 , respectively when heated with carbon above 1,800°C

Uranium dissolves rapidly in nitric and hydrochloric acids. With hydrochloric acid, a black residue often remains. In sulfuric, hydrofluoric, and phosphoric acids, the metal dissolves slowly. Uranium is not affected by alkalies.

Uranium reacts with boiling water forming its dioxide, UO_2 , and evolving hydrogen. The hydrogen produced combines with metal to form hydride.

Uranium reacts with dinitrogen tetroxide, N_2O_4 , in acetonitrile to form an intermediate, $UO_2(NO_3)_2 \cdot N_2O_4 \cdot 2CH_3CN$, which on heating above 160°C yields uranyl nitrate, $UO_2(NO_3)_2$.

Analysis

Radioactivity of uranium can be measured by alpha counters. The metal is digested in nitric acid. Alpha activity is measured by a counting instrument, such as an alpha scintillation counter or gas-flow proportional counter. Uranium may be separated from the other radioactive substances by radiochemical methods. The metal or its compound(s) is first dissolved. Uranium is coprecipitated with ferric hydroxide. Precipitate is dissolved in an acid and the solution passed through an anion exchange column. Uranium is eluted with dilute hydrochloric acid. The solution is evaporated to near dryness. Uranium is converted to its nitrate and alpha activity is counted. Alternatively, uranium is separated and electrodeposited onto a stainless steel disk and alpha particles counted by alpha pulse height analysis using a silicon surface barrier detector, a semiconductor particle-type detector.

Hazard

Uranium and its compounds are highly toxic. These substances also present a radiation hazard. Finely-divided metal is pyrophoric.